Properties of Amorphous Si

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Properties of Amorphous Si : H Films Prepared by Dual Ion Beam Sputtering

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Abstract

The Ion Beam Sputtering (IBS) and the Dual Ion Beam Sputtering (DIBS) allow independent control of the deposition kinetics and the hydrogenation of hydrogenated amorphous silicon (a-Si : H) films. This makes it possible to investigate the correlations between the disorder in the amorphous matrix and the optical parameters, such as optical gap and Urbach energy. Data were taken for samples grown at different substrate temperatures, having different hydrogen content, or presenting damage induced by argon bombardment. In addition, an experimental evaluation of the shift in optical gap due to the alloying with H was carried out and gave 6.63×10^{-3} eV/at %.

Thin a-Si : H films ($\sim 1\,\mu$m) have been prepared by dual ion-beam sputtering (DIBS) [1]. The deposition apparatus is shown in Fig. 1: a beam of argon is used to sputter silicon from a polycrystalline target to a heated substrate, while a beam of hydrogen impinges directly onto the growing film. This technique allows independent control of the deposition kinetics and the hydrogenation of the film since the latter is determined by the current and the voltage of the hydrogen gun. The DIBS apparatus can also be used to enhance the structural disorder present in the sample through bombardment of the growing film by other species, e.g., argon.

The samples have been deposited at two different substrate temperatures: 200°C and 300°C. Care has been taken to avoid residual metallic contamination of the deposited material deriving from the sputtering of the walls of the deposition chamber [2]: a silicon screen was applied to the target and the argon beam was surrounded by a silicon tube acting as a collimator.

The hydrogen content (C_H) of the samples was deduced from optical transmission measurements in the IR region and turned out to vary between 3 and 22 at %.

The optical gap (E_g) of every film was determined from Tauc plots of the optical absorption coefficient in the region $2.0 \leqslant E \leqslant 2.5$ eV. The results show a correlation between the hydrogen content and E_g (see Fig. 2): for a substrate temperature of 200°C $E_g = 1.38$ eV for $C_H = 0$, while increasing up to a value of 1.78 eV when $C_H = 18$ at %, consistent with the fact that hydrogen lowers the degree of disorder in the sample. For higher hydrogen content the gap stops increasing and seems instead to decrease consistently with the hypothesis that the compositional disorder introduced by the hydrogen opposes and eventually overwhelms the decrease in structural disorder. In fig. 3 we show E_g vs. C_H for samples deposited at 300°C with and without additional Ar-bombardment of the growing film. In the bombarded samples E_g drops to much lower values as $C_H \to 0$. Since the chemistry is the same, this indicates that severe structural imperfections are now the dominant factor [3]. Samples prepared by IBS [1] in hydrogen atmosphere show an E_g vs. C_H behavior similar to the Ar bombarded DIBS samples (see squares in Fig. 3). This emphasizes the advantage of using energetic hydrogen in regard to its "healing effect" on the structural disorder of the films.

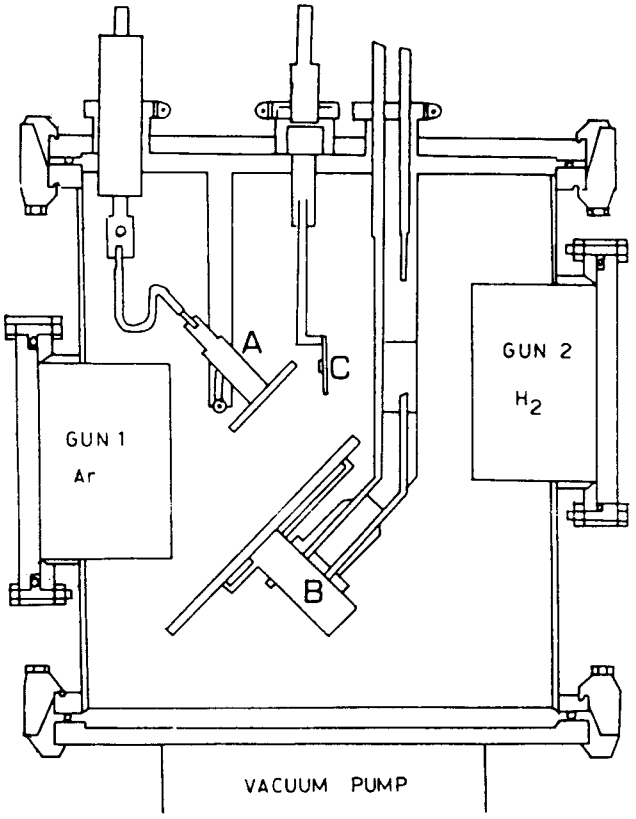

Fig. 1. Schematic diagram of the DIBS apparatus; A heates substrate holder, B polycrystal target, C electrical probe.

In order to be able to quantify the relationship between the optical gap and the disorder, the Urbach edge parameter E_0 was deduced. This parameter – as is well known – corresponds to the extention of the valence band tail and has been determined from spectral photoconductivity and photothermal deflection spectroscopy measurements. These measurements give the absorption coefficient, $\alpha = \alpha_0 \exp(-h\nu/E_0)$, in the near gap region. The typical E_0 value for our samples was ~ 60 meV indicating that the growth parameters are optimized and that the DIBS technique allows one to produce films with approximately the same degree of disorder present in material deposited with the more commonly used glow-discharge technique.

In order to describe both E_0 and E_g in terms of disorder, the sums of the mean quadratic deviations W^2 of the potential about the ideally ordered structure due to structural,

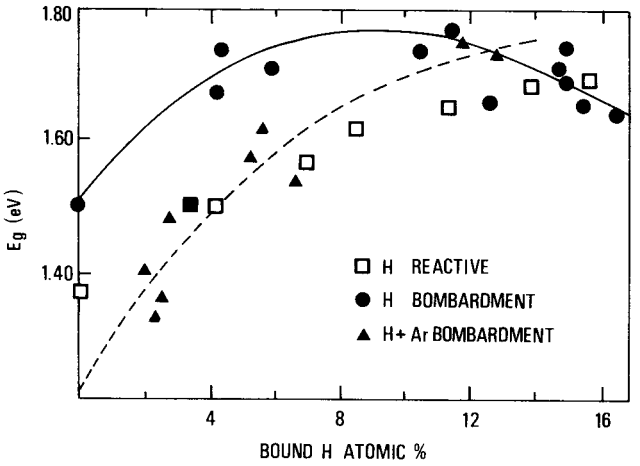

Fig. 2. Plot of E_g vs. bounded hydrogen concentration for samples deposited at 300°C with (full triangle) and without (full circle) additional Ar bombardment of the growing film. Also shown (full square) is the behavior of a sample deposited by shutting off the H-gun and sputtering in H atmosphere (H reactive) and of samples (open square) grown in the same way be Saraie *et al.* [1].

thermal and compositional disorder have to be introduced [3, 4]:

$$E_0 = K_0(W_X^2 + W_T^2 + W_H^2) \quad (1)$$

$$E_g = E_x + \Delta E_x - K_g(W_X^2 + W_T^2 + W_H^2) \quad (2)$$

with K_0, K_g constants and E_x representing the ideal optical gap of the sample with no disorder. ΔE_x corresponds to the chemical effect of hydrogen on the ideal optical gap, i.e. to the modification of the band structure resulting from the presence of a certain number of Si-H bonds.

The chemical effect has been assumed neglectable by Cody *et al.* [3] up to hydrogen contents of the order of 20 at %. We are in the position to verify this assumption. By comparing two samples deposited at different temperatures, but having the same hydrogen content (12 at %), and therefore the same E_x, we write

$$\Delta E_0 = E_{01} - E_{02} = K_0(W_{X1}^2 - W_{X2}^2)$$

$$\Delta E_g = E_{g1} - E_{g2} = K_g(W_{X1}^2 - W_{X2}^2)$$

The terms in W_T disappear in the subtraction because the values of E_0 and E_g were all determined at the same temperature. Therefore we have

$$\Delta E_g/\Delta E_0 = -K_g/K_0 = -6.25$$

This value is in good agreement with the one found by Cody et al. [4]: $K_g/K_0 = 6.2$. Similar results are obtained for

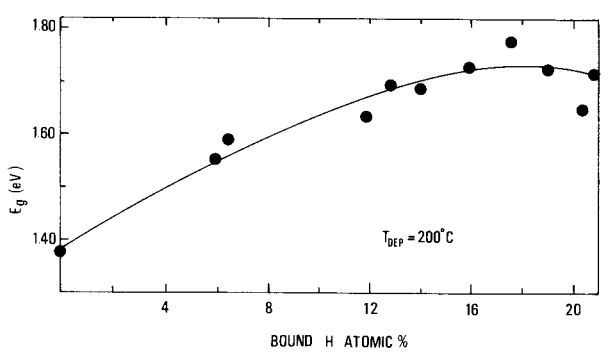

Fig. 3. Plot of E_g vs. bounded hydrogen concentration for samples deposited at 200°C.

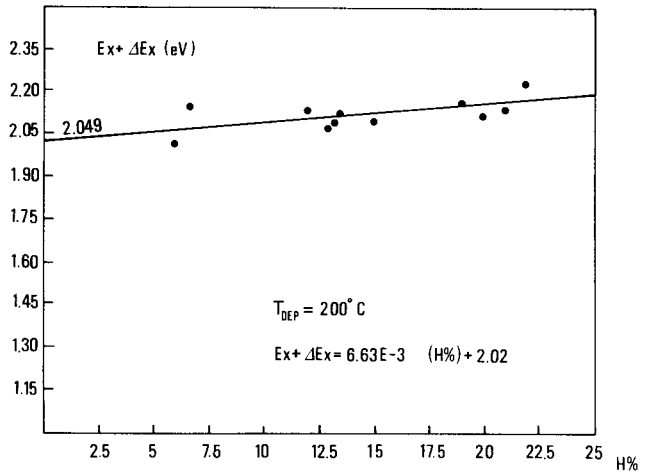

Fig. 4. Plot of $E_g + (K_g/K_0)E_0 = E_x + \Delta E_x$ vs. bound hydrogen concentration for samples deposited at 200°C. From the plot there result an ideal optical gap $E_x = 2.02$ eV and a chemical shift of E_g due to the alloying with hydrogen $\Delta E_x = 6.63 \times 10^{-3}$ eV per at % H.

different pairs of samples, chosen in a way that their differences in E_g and E_0 are appreciately larger than the experimental error.

We now take the vlues for E_0 and E_g measured for the films deposited at a substrate temperature of 200°C and plot

$$E_g + (K_g/K_0)E_0 = E_x + \Delta E_x$$

as a function of hydrogen content. We find an ideal optical gap $E_x = 2.02$ eV and a chemical shift $\Delta E_x = 6.63 \times 10^{-3}$ eV per at % of hydrogen (see Fig. 4). This is the first experimental determination of the increase of the optical gap due to the chemical effect of hydrogen only. It leads to an increase of 135 meV for $C_H = 20$ at %, which corresponds to about half of the theoretical estimate [5].

This analysis neglects another possible contribution to E_g: the effect of the density of the film on the optical gap. This effect should be small compared to the measured differences in E_g for the different samples, but it is hard to quantify and up to date no measurements are available.

The density of gap states N_8 has been deduced from the profile of the absorption coefficient at low photon energies, as obtained by photoconductivity measurements. We found N_8 of the order of 10^{16} cm^{-3}. This result shows that the DIBS technique produces films with a density of gap states comparable to the one reported in literature for materials with good photoelectronic properties [6, 7].

Quite to the contrary, our material exhibits $\mu\tau$-product and photoconductivity values (respectively $\simeq 2 \times 10^{-9}$ cm^2/V and $1 = 10^{-9}\,\Omega^{-1}$ cm^{-1} at 10^{15} photons s^{-1} cm^{-2}) which are considerably lower than those of glow-discharge samples [8, 9]. Dark conductivity measurements as a function of temperature gave activation energies higher than 0.7 eV. This means that our samples have the Fermi level in the lower half of the gap, which accounts for the observed $\mu\tau$ values [10].

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